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Short Communication

Formation and UV-Vis Studies of Lead Sulfide Nanoparticles

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An elegant technique of synthesizing semiconductor lead sulfide nanoparticles (PbS-NPS) embedded in Langmuir-Blodgett (LB) films is presented here. Stearic acids have been used as a matrix to form and grow the quantum-sized PbS. Pure Y-type Pb-salts of stearic acid (SA) LB films were prepared at a dipping speed of 15 mm/min and surface pressure of 28 mN/m. PbS-NPs were formed inside LB films of SA by exposure the LB films to hydrogen sulfide (H₂S) gas. The preparation of PbS-NPs is discussed in terms of particle formation and growth. The presence of PbS-NPs was investigated by UV-visible absorption. It was found that the PbS-NPs within SA LB films indicated a large blue shift of the optical absorption edge. The estimation of the size distribution performed by optical measurements allows one to attribute the particle range a few nanometers. This figure seems to depend upon the reaction conditions as well as the quality of the initial LB films.

Keywords: LB films, PbS-NPs, Quantum confinement, Energy gap.

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1. INTRODUCTION

Quantum-sized semiconductor materials have been an active area of research due to their unique electronic and optical properties. PbS is one of the most studied materials among the II-VI compounds. As we know, the fabrication of all wide-band-gap semiconductors, such as lead sulfide, was conducted by molecular beam epitaxy (MBE) techniques and metal organic chemical vapor (MOCVD) deposition. These techniques require a high-vacuum system and high temperature processing, and costly expensive facilities. On other hands, wide band gap semiconductor materials have been intensively investigated using relatively simple techniques and synthesized by quantum size semiconductor [1, 2].

Today, quantum dots and nanocrystals have recently implemented for variety of optoelectronic applications, such as photodetectors [3], light-emitting diodes [4, 5] and solar cells [6-8]. Lead chalcogenide colloidal quantum dots based photodetectors can be obtained by spin-coating, dip-coating, or drop-casting techniques on a rigid or flexible substrate [9].

In this way, an elegant method for the formation of quantum state and metal particles in Langmuir-Blodgett films has been reviewed [10]. This technique has now become very promising for the formation of various nanostructures for electronic device applications. The technology of ordered organic films, particularly LB films, gives many opportunities to control the size of nanoparticles and formed ordered organic-inorganic systems and provides a real alternative for costly molecular beam epitaxy (MBE) technology.

We supposed that small PbS-NPs might be formed inside SA LB films and their absorption spectra are blue shifted in respect to the bulk PbS materials by ~ 0.41 eV. Some researchers reported that the considerably large

average distance between the electron and the corresponding created hole under the effect of Coulomb binding is ~ 18 nm [11] and ~ 46 nm [12] (i.e., bulk exciton Bohr radius). UV-VIS absorption spectroscopy is a useful technique to monitor the optical properties of the quantum-sized particles. The wavelength at the maximum exciton absorption decreased as the size of the nanoparticles decreased as a result of quantum confinement of the photogenerated electron-hole carriers [13]. Methods for the quantitative evaluation of particle size in thin LB films based on the analysis of ultra violet reflection absorption and transmission intensities have been developed. Ref. [14] reported an approach to converting a measured absorbance spectrum (λ) and the corresponding TEM images for PbS-QDs into a relationship between band gap (E_g) and particle size x . According to these results, it is confirmed that for PbS-QDs a validated size range is from 3 to 7 nm derived from the absorbance spectra in order to determine the band gap energy versus particle size relationships. A comprehensive overview of the quantitative analysis of PbS-QDs light absorption by the Maxwell-Garnett (MG) effective medium theory has been investigated [15]. This theory predicts the strong enhancement of the absorbance at above 3.5 eV is related to marked increase in the local field factor.

The focus of this work is to study the formation and optical characterization of PbS-NPs by cycles of immersion in a solution containing appropriate Pb metal cation in stearic acid (SA) and exposure to H₂S gas.

2. EXPERIMENTAL

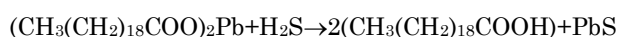
2.1 Formation of PbS-NPs LB Films

The stearic acids (C₁₇H₃₅COOH) were chosen as monolayers of LB films. The water used for subphase solutions

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was purified by Milli-Q system (Millipore Corp. Ltd.). Monolayers of stearic acids were formed by spreading 1 mg/mL solution of the compounds on the surface of pure water (pH 5.3) containing $5 \cdot 10^{-4}$ M $\text{Pb}(\text{NO}_3)_2$ in a commercial 622A series LB-trough of NIMA Technology Ltd., England. The monolayers were compressed at a speed of 20 mm²/s up to a surface pressure of 28 mN/m. Y-type (even number) of LB films were transferred onto a solid hydrophobic substrate (glass slide) by a vertical dipping technique at a deposition speed of 15 mm/min for both down- and upstroke with the film balance and a lifter (NIMA Technology Ltd.).

Glass slides were cleaned in chromatic acid to remove organic contamination and then rinsed several times in pure water with ultrasonic action. The substrates were made hydrophobic by treatment overnight with hexamethyldisilazane $[(\text{CH}_3)_3\text{Si-NH-Si}(\text{CH}_3)_3]$ vapor. In this study, we have grown two samples with different PbS-NPs layer deposition (i.e., 10 and 20 layers). PbS NPs in the stearate LB matrix were formed by exposure the SA LB films to a flow of H_2S gas for a few hours at room temperature according to the reaction:



2.2 Optical Characterization of PbS-NPs LB Films

Absorption spectra of the SA LB films transferred to glass slides were characterized after exposure to H_2S using a Unicam UV-vis spectrometer UV4. UV-Vis absorption spectrum was recorded and analyzed for PbS-NPs films at room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 shows schematic representations of the PbS-NPs LB film formation grow to the glass substrate.

Classical LB films of metal salts of fatty acid, including Pb-salts SA LB films, can be made by attraction ion from surface of subphase containing Pb- salts. When the LB films are exposed to H_2S gas, PbS-NPs semiconductor is formed inside each bilayer of LB films as shown

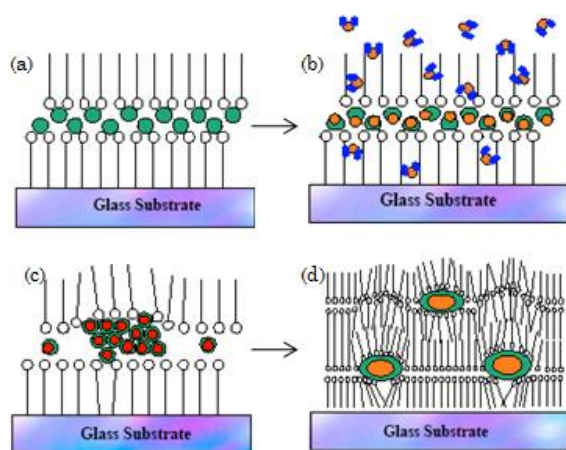


Fig. 1 – Formation of PbS-NPs in SA LB films: (a) formation of SA LB films containing Pb salts, (b) reduction of the metal within LB film by exposure to H_2S . Segregation and formation of PbS clusters in LB films: (c) segregation of 2D-layers of PbS and formation of PbS clusters and (d) PbS-NPs formed within SA LB films

in Fig. 1a, b. These semiconductor layers segregate and form clusters of PbS-NPs semiconductors. The process may start from small clusters of PbS-NPs of a few molecules and then the molecules interact with other molecules and the clusters of PbS-NPs grow bigger in order to reduce surface energy. LB monolayer transfer occurs on both down stroke and upstroke, head-to-head and tail-to-tail orientations of the monolayers are achieved [16]. As a result, larger particles (a few nanometers in diameter) are formed inside each bilayer of LB films (Fig. 1c, d). Because of the limit of the material in the films, when PbS-NPs are formed, the order of the layer-by-layer film reduces and the thickness of the films increases. Lead chalcogenide CQDs can also be self-assembled into regular arrays [17].

Typical UV-visible absorption spectra of PbS-NPs in SA LB films (10 and 20 layers) are shown in Fig. 2. The wavelength of the first exciton peak increases from 400 to 600 nm. The spectra show two well resolved bands related to the presence of PbS-NPs in the LB films. These peaks correspond to the $1\text{S}_e-1\text{S}_h$ and $1\text{S}_e-1\text{P}_h$ transitions, respectively. An indirect transition involves the meeting of three particles: an electron, a photon and a phonon. This means that the indirect transition is a less probable process than the direct.

To determine the band gap, Fig. 3 shows the plot of $(\text{Abs}/N)^2$ as a function of photon energy for PbS-NPs films linear in the region of the strong absorption zone near the absorption edge. This means that optical transition takes place directly. The intercepts of the extrapolated straight line at the $(\text{Abs}/N)^2 = 0$ axis give the values of the band gap energy (E_g) of ~ 2.4 eV.

Fig. 4 shows the absorption of PbS-NPs via altering the particle size from 3 nm to 3.5 nm, and the excitonic maxima ranging from 400 nm to 600 nm can be realized, corresponding to the bandgap from 2 to 1.98 eV. In practice, the absorption threshold exhibits the explicit relationship between the particle size diameter curve and the first exciton absorption peak (E_g), corresponding to $1\text{S}_e-1\text{S}_h$ and $1\text{S}_e-1\text{P}_h$ transitions) [18]. The particle size has been measured by TEM and is 2.8 nm and it is in good agreement with the size calculated from its absorption spectrum 2.7 nm for 870 nm exciton peak [19]. The hollow PbS nanospheres have been studied and show that the diameters of 12 nm are synthesized by sonochemical route [20].

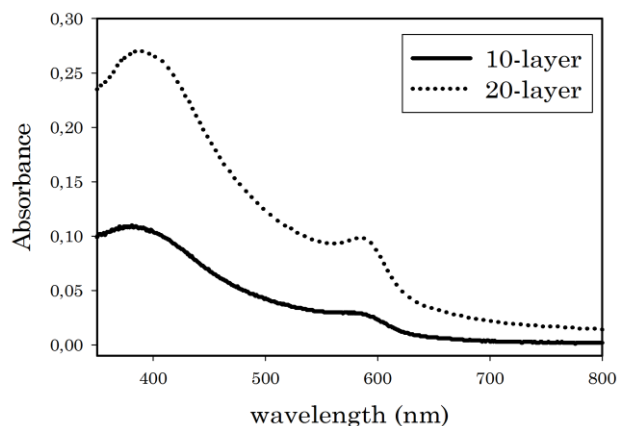


Fig. 2 – UV-visible absorption spectra of PbS-NPs in SA LB films. The measurement temperature is 300 K

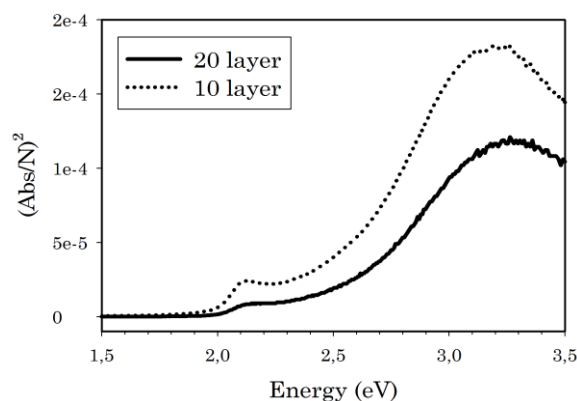


Fig. 3 – Abs/N squared vs variation of photon energy

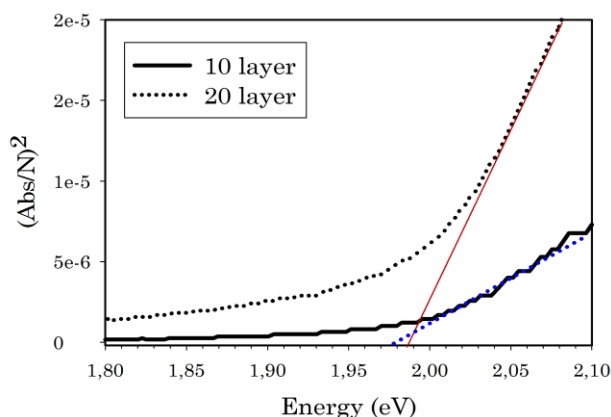


Fig. 4 – Abs/N squared vs variation of photon energy

The absorption edge of PbS-NPs is considered within the range of 1.98-2 eV (visible region) blue shift in respect to the bulk material (near-infrared region), as seen from Fig. 4. A bulk property of PbS-NPs is a narrow direct band gap semiconductor of about 0.41 eV [11]. Due to the large Bohr radius of the exciton in the bulk (about 18 nm), reduction of particle size in the range of 3.0-3.5 nm, oppose strong quantum confinement. Other workers have also reported the blue shift indicating that PbS exists as small clusters within the QDs materials [1-3, 7]. According to the literature [17], the average diameter of PbS QDs was estimated to be about 7 nm, it corresponds to the band-gap of the PbS QDs $E_g = 0.9$ eV. Hence, we remarked that LB technique is essential to have a better under-standing of particle growth formation and becomes guideline to control particle size modification to improve optical properties for further applications.

4. CONCLUSIONS

PbS-NPs semiconductors are formed inside each bilayer of LB films after exposing the LB films to H_2S gas. The UV visible absorption spectra analysis of the obtained results shows a substantial blue shift (up to 1.98 eV) with a decrease in the particle size. It has confirmed the formation of PbS-NPs of 3-3.5 nm size in the LB film.

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Формування та УФ дослідження наночастинок сульфідів свинцю

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У роботі представлена оригінальна методика синтезу напівпровідникових наночастинок сульфиду свинцю (PbS-NPS), вбудованих в плівки Ленгмюра-Блоджетт (LB). Стеаринові кислоти використовувалися як матриця для формування та вирощування квантоворозмірного PbS. Чисті Pb-солі Y-типу плівок LB стеаринової кислоти були приготовані при швидкості занурення 15 мм/хв і поверхневому тиску 28 мН/м. PbS-NPs формувалися всередині плівок LB стеаринової кислоти шляхом опромінення плівок LB сірководневим (H_2S) газом. Підготовка PbS-NPs обговорюється з точки зору утворення і росту частинок. Наявність PbS-NPs досліджували за допомогою УФ та видимого поглинання. Було виявлено, що PbS-NPs в плівках LB стеаринової кислоти вказують на великий синій зсув краю оптичного поглинання. Оцінка розподілу розмірів, виконана за допомогою оптичних вимірювань, дозволяє віднести діапазон частинок до кількох нанометрів. Ця цифра залежить від умов реакції, а також від якості вихідних плівок LB.

Ключові слова: Плівки LB, PbS-NPs, Квантова локалізація, Енергія забороненої зони.